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ARTICLE

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Melt spinnability of long chain cellulose esters

Pia Willberg-Keyriläinen[1] | **Teijo Rokkonen**[2] | **Tero Malm**[2] | **Ali Harlin**[1] | **Jarmo Ropponen**[1]

[1]VTT Technical Research Centre of Finland Ltd, Espoo, Finland

[2]VTT Technical Research Centre of Finland Ltd, Tampere, Finland

Correspondence
Pia Willberg-Keyriläinen, VTT Technical Research Centre of Finland Ltd, Tietotie 4E, PO Box 1000, Epsoo 02044, Finland.
Email: pia.willberg-keyrilainen@vtt.fi

Abstract

Technical and hygienic nonwovens, originating typically from fossil-based synthetic polymers, are the fastest growing applications in the textile industry. Recently developed thermoplastic cellulose fatty acid esters have polyolefin like rheology properties and therefore the suitability of these cellulose esters for fiber production was evaluated. In this study, the melt spinning of textile fibers has been demonstrated using thermoplastic cellulose octanoate. The mechanical properties of melt spun fibers were analyzed by using tensile testing and both the surface and cross-section morphology of melt spun fibers were studied using the scanning electron microscopy. The surfaces of the fibers were very smooth and also the cross-section was very uniform and no porosity was observed. While mechanical properties of the produced fibers are not yet as good as those reported for commercial polypropylene (PP) monofilament fibers, they are somewhat more comparable to other cellulose ester-based fibers. The melt spinning results indicate that the novel cellulose-based fibers can provide a renewable and recyclable alternative, for example, spun-laid PP in several hygienic textile and fully oriented in technical applications in future.

KEYWORDS

biomaterials, cellulose and other wood products, fibers, thermoplastics

1 | INTRODUCTION

Currently, the global market of nonwoven products is continuously growing and so far polypropylene (PP) and polyester (poly(ethylene terephthalate) [PET]) as raw materials have dominated the nonwoven industry.[1,2] The interest in new materials based on renewable resources has grown in recent years due to environmental concerns. However, bio-based materials still have a minimal fraction of the total global plastic market.[3]

Melt spinning process is one of the most convenient methods for polymer fiber manufacturing at an industrial scale for the textile industry.[4,5] Polyesters (e.g., PET), polyamides (e.g., nylon 6), and PP are typical synthetic polymers that can be converted through melt spinning into fibers.[6–8] Melt spinning is a simple process, which offers many advantages compared with solvent or wet-fiber spinning, such as no solvents are needed, there are no toxic byproducts, and the production speed is high.[9–11]

In melt spinning process, the used polymer has to be thermoplastic,[6] therefore pure cellulose is not directly processable by melt spinning. Thermoplastic behavior of cellulose can be improved, for example, by using esterification.[12,13] Only a few results of cellulose-based melt spinning fibers, which have been prepared using cellulose

acetate butyrate (CAB), have been reported earlier.[4,10,14,15] However, plasticizers (e.g., triethyl citrate [TEC], polyethylene glycol) are required for all these reported short chain cellulose derivatives. In our previous studies, we have developed a thermoplastic long chain cellulose esters,[12,13,16] which are processable without the addition of a plasticizer. In the previous studies, we have shown the suitability of long chain cellulose esters for extrusion and injection molding. However, the suitability of this material for melt spinning process has not been tested earlier. The rheological behavior of the material in melt spinning has to be well controlled, including die swell and elongational viscosity, closely related to the molar mass, its distribution, and evenness of the material.

In this study, the melt spinning process of thermoplastic cellulose esters has been studied. The molar mass controlled long chain cellulose esters with different side chain length were synthesized with different degrees of substitution (DS), and the suitability of these cellulose esters for fiber production was evaluated. To see the differences in thermal behaviors, capillary rheometer tests were conducted and according to these results, the best cellulose ester was chosen for larger scale melt spinning tests. In larger scale melt spinning tests (Figure 1), cellulose octanoate fibers were spun using different drawing speeds (60–200 m/min) and the mechanical properties (e.g., tenacity and elongation) of fibers were analyzed. Also, the effect of avivage (postsizing) agent on fiber properties was studied.

2 | EXPERIMENTAL

2.1 | Materials

The cellulose materials for esterification were commercial softwood dissolving grade pulp produced by Domsjö Fabriker AB (Sweden) and the pulp was ozone pretreated according to a method described by Willberg-Keyriläinen et al.[12] PP (HF420FB, Borealis, Finland) was used as the reference material during the rheometry. Commercial Tallopol SLB (Bozzetto, Italy) was used as an avivage agent. All other reagents and solvents were purchased from Sigma-Aldrich (Helsinki, Finland) in the highest purity grade available and were used as received.

2.2 | Methods

2.2.1 | Preparation of cellulose esters

The homogenous esterification of the cellulose was conducted using the method presented by Willberg-Keyriläinen et al.[12,13] In this method, dry cellulose was first dissolved in a 5% lithium chloride/N,N-dimethylacetamide [LiCl/DMAc] solution. Then, fatty acid chloride (hexanoyl chloride [C6], octanoyl chloride [C8], lauroyl chloride [C12], or palmitoyl chloride [C16], 3 or 4 equivalents to cellulose anhydroglucose unit [AGU]) was added to the cellulose mixture using pyridine (3.6 or 4.6 equivalents/AGU) as a catalyst. The reaction temperature was 80°C and reaction time 16 hr. The product was precipitated with ethanol and washed with ethanol and acetone.

2.3 | Solid state nuclear magnetic resonance

The cellulose esters were analyzed using solid state ^{13}C cross polarization / magic angle spinning nuclear magnetic resonance spectroscopy (^{13}C CP/MAS, ssNMR). Analyses were carried out using an Agilent 600 MHz NMR spectrometer (Agilent Technologies). All ssNMR experiments were carried out at 22°C using MAS rate of 10 kHz, 10,000 scans, and 10 s recycle time.

2.4 | Thermal gravimetric analysis

The degradation temperatures ($T_{deg,10\%}$) of cellulose esters were investigated with thermal gravimetric analysis (TGA) (Netzsch STA449F1, Netzsch Gerätebau GmbH, Germany). The TGA measurements were carried

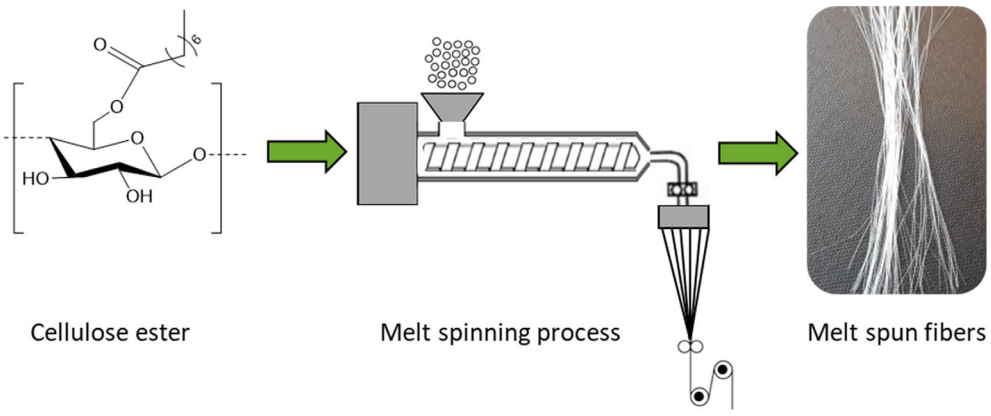

FIGURE 1 Schematic illustration of this research [Color figure can be viewed at wileyonlinelibrary.com]

out in air atmosphere from 40 to 600°C with a heating rate of 10°C/min.

2.5 | Capillary rheometer

The spinnability of prepared cellulose esters was first evaluated with Göttfert Rheograph 6000 capillary rheometer (Göttfert, Germany). The capillary rheometry was carried out by using a 1/30 mm die and shear rates of 30, 100, 200, 300, 600, and 1,000 s^{-1}. Tests were performed at 130°C with 3 min preheating time. If the material did not produce fiber like structure at 130°C, the temperature was raised until the material produced fibers or degraded. Apparent values were recorded and spinnability was assessed by hand. The viscosity data were fitted with Carreau–Yasuda equation[17] for visualization purposes. Prior to experimenting, the materials were dried in ambient vacuum overnight.

2.6 | Melt spinning

Melt spinning was performed using a Fourné melt spinning machine (Fourné Polymertechnik GmbH, Germany) consisting of a 10 mm single screw extruder (rate 100 rpm), melt pump (rate 14 rpm), and multistrand filament die. The spinneret with eight holes (diameter of 0.7 mm) was used. Spinning was performed at 130°C and the produced fibers were air-cooled. The melt spun fibers were collected on a godet and melt-oriented using a drawing speed range of 0–200 m/min with and without an avivage agent. The raw material was dried at ambient vacuum over night before processing.

2.7 | Scanning electron microscopy

Scanning electron microscopy (SEM) analysis of the melt spun fibers was carried out using a field emission SEM (MERLIN FE-SEM, Carl Zeiss GmbH, Germany). The 3 kV acceleration voltages were used and prior to imaging, the samples were sputter-coated (Leica EM ACE200, Germany) with a thin gold layer. For cross-section imaging, the fibers were freeze-fractured under liquid nitrogen. Five replicate fibers were used in measuring the mean diameter ($n = 5$).

2.8 | Tensile testing of fibers

Mechanical properties of melt spun fibers (cellulose octanoate, DS = 1.4) were analyzed using a Favimat+ testing system (Textechno, Germany) with a load cell of 210 cN, gauge length of 20 mm and constant rate crosshead speed of 20 mm/min. Twenty replicate fibers were tested and the fibers were kept in standard conditions (23°C, 50% relative humidity) for 1 week before testing. The linear density of the undrawn fiber was above the maximum limit of the Favimat+ machine. Therefore, tensile testing of undrawn fiber was performed with Instron 4505 universal material tester (Instron Corp.) using 100 N load cell, gauge length of 20 mm, and similar 20 mm/min extension rate.

2.9 | Statistical analyses

The statistical analyses were performed using the SPSS (SPSS Statistics Software 24.0, IBM) for the results with a minimum of five replicates. The significant differences were analyzed using one-way analysis of variance with the Tukey HSD test.

3 | RESULTS AND DISCUSSION

3.1 | Preparation of cellulose esters

Cellulose esters were prepared with different side chain lengths (C6–C16) according to our earlier study[13] and the DS of the cellulose esters was analyzed using solid state NMR spectroscopy by comparing the cellulose esters carbonyl carbon (175 ppm) integrals with the cellulose C1 signal (105 ppm) integral. The ssNMR spectrum of cellulose octanoate (Entry 5) with signal assignation is presents in Figure 2. According to the ssNMR, the DS

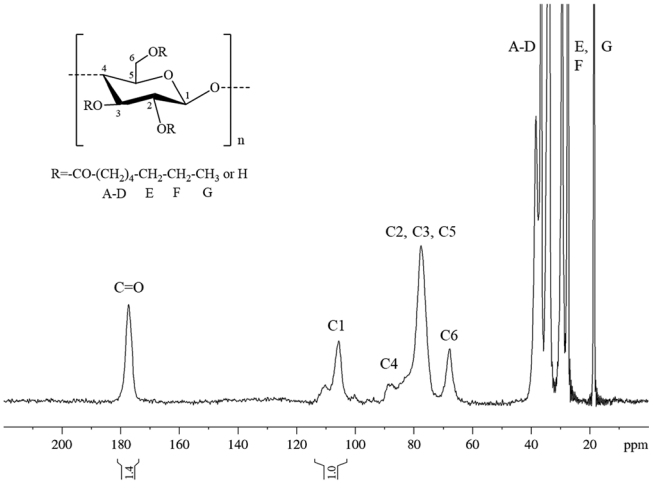

FIGURE 2 Solid state nuclear magnetic resonance (ssNMR) spectrum of the cellulose octanoate degree of substitution (DS) 1.4 (Entry 4)

TABLE 1 Degree of substitution, degradation temperatures, testing temperatures, and spinnability assessments of prepared cellulose esters

Entry	Cellulose ester type	Acyl chloride (eq./AGU)	DS[a]	$T_{deg,10\%}$ (°C)	Testing temperature (°C)	Spinnable
1	Hexanoate, C6	3	1.3	297	130–140	No
2	Hexanoate, C6	4	1.5	301	130	Yes
3	Octanoate, C8	3	1.0	290	130–160	No
4	Octanoate, C8	4[b]	1.4	308	130	Yes
5	Octanoate, C8	4	1.5	293	130	Yes
6	Laurate, C12	3	1.1	241	130–140	No
7	Palmitate, C16	3	1.0	260	130–160	No
8	Palmitate, C16	4	1.2	274	130–150	No

Abbreviation: AGU, anhydroglucose unit.
[a]According to solid state nuclear magnetic resonance (ssNMR), error limit ±0.1.
[b]Synthesized in bench scale (3 kg/batch).

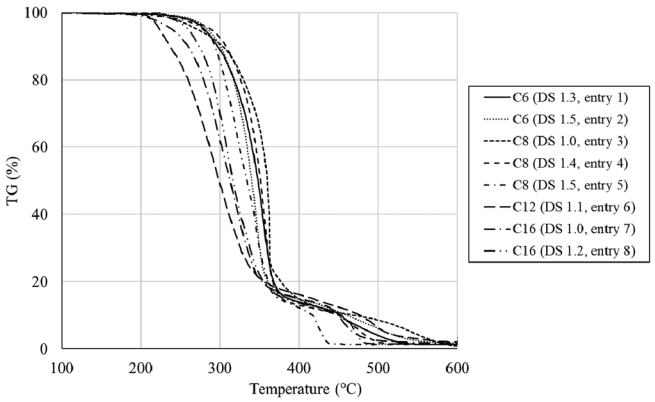

FIGURE 3 Thermal gravimetric analysis (TGA) curves of cellulose esters. DS, degree of substitution

values ranged from 1.0 to 1.5 and results are given in Table 1. We have previously reported,[13,16] that the side chain length significantly affects the mechanical properties of cellulose esters. For example, five times higher elongation values have been reported for cellulose C8 ester compared with cellulose C16 esters.[16] These cellulose esters are also 100% bio-based materials, which can be processed without any plasticizer.

3.2 | Rheological measurements

The rheological measurements (capillary rheometer) were conducted for prepared cellulose esters to see the suitability of these esters for fiber production. The testing temperatures and spinnability assessments are given in Table 1. When the narrow rheometer extrudate formed a thin monofilament without breaking when pulled by hand, the material was marked as spinnable. If the material did not flow out of the rheometer or the extrudate broke when pulled at the initial 130°C, the temperature was increased by 10°C (without refilling) until the material was able to flow out from the rheometer or thermally degraded (dark color). However, in this case, the material was marked as unspinnable. It is well known that high temperatures cause thermal degradation of cellulose,[10,18] therefore the processing temperature should be much lower than degradation temperature. Degradation temperatures ($T_{deg,10\%}$) of these long chain cellulose esters are between 241 and 308°C, which are in line with earlier reported values.[12,19,20] Moreover, the decomposition temperatures of all materials are clearly higher than the used temperatures in melt spinning process. The total TGA curves are presents in Figure 3.

According to the rheological measurements, only cellulose hexanoate (Entry 2, DS 1.5) and cellulose octanoates (Entry 4, DS 1.4 and Entry 5, DS 1.5) were spinnable (Figure 4) at tested 130°C conditions. These materials had the best melt flowing characteristics and produced the most stable extrudates without melt fracture. These esters had the highest DS values, which may thus have an effect on the fiber formation. It is earlier reported[13,21] that DS decreases when side chain length of cellulose ester increases in similar reaction conditions due to the steric hindrance, and therefore the DS values of longer side chain cellulose esters are lower than values of shorter side chain esters.

It is necessary that the material have suitable melt properties for filament production. Melt viscosity is the most important parameter. The viscosity of cellulose hexanoate (Entry 2) and cellulose octanoates (Entry 4 and Entry 5) were measured using different shear rates and their behavior was compared with the PP reference material (Figure 5). The DS value seems to have a big

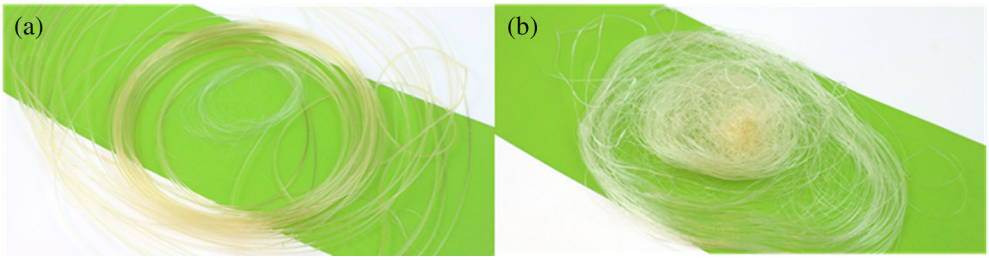

FIGURE 4 (a) Cellulose hexanoate degree of substitution (DS) 1.5 (Entry 2), and (b) cellulose octanoate DS 1.5 (Entry 5) as produced by the capillary rheometer [Color figure can be viewed at wileyonlinelibrary.com]

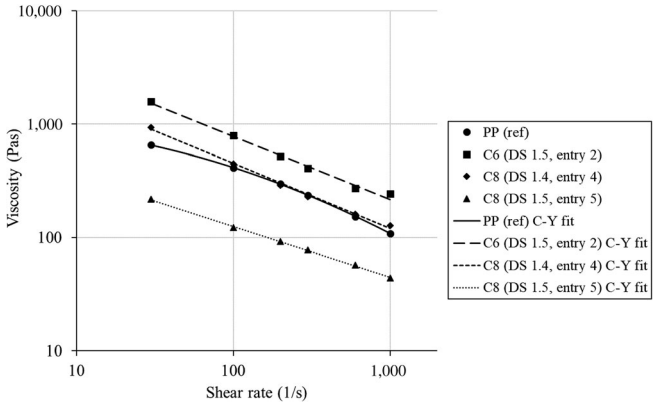

FIGURE 5 Capillary rheometer test for cellulose hexanoate and cellulose octanoates compared to polypropylene reference. Data fitted with Carreau–Yasuda Equation (C–Y). DS, degree of substitution; PP, polypropylene

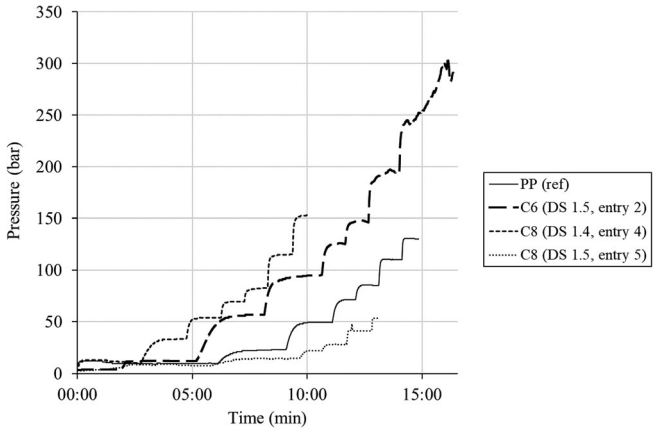

FIGURE 6 Pressure behavior during capillary rheometer measurements. Each step in pressure represents change in shear rate. DS, degree of substitution; PP, polypropylene

effect on viscosity values. Cellulose octanoate with DS 1.4 (Entry 4) has very similar viscosity behavior to PP, while cellulose octanoate with DS 1.5 (Entry 5) has significantly lower viscosity. Cellulose hexanoate (Entry 2, DS 1.5) with lower side chain length has notably higher viscosity than cellulose octanoate with same DS; therefore, the side chain length has a major effect on viscosities.

The pressure behavior during the capillary rheometer measurements is presents in Figure 6. The pressure behavior shows the stability of the polymer flow and how fast the rheometer was able to find a stable pressure value before proceeding to the next shear rate. It can be seen that both cellulose octanoate variants behaved very similarly to the reference PP, that is, pressure was stable with almost every shear rate step. Cellulose octanoate with DS 1.4 (Entry 4) was also slightly faster to complete the measurement than DS 1.5 (Entry 5), which to some extent indicates that its melt flow stabilized more quickly. Nevertheless, while cellulose hexanoate was regarded as spinnable, it had some unstable flow behavior at high shear rates, which can be seen as an uneven pressure response.

3.3 | Larger scale melt spinning process

Based on the rheological measurements, the cellulose octanoate with DS 1.4 (Entry 4) was considered the most promising material, and thus selected for additional larger scale melt spinning experiments. The target was to study in detail the melt spinnability of cellulose octanoate using a Fourné melt spinning machine. In the melt spinning process, the influence of the fiber drawing speed on the mechanical properties of the resulting fibers was studied. Therefore, the drawing speed was varied from 0 to 200 m/min. In addition, the effect of an avivage agent on the fiber properties was tested using 10% Tallopol SLB (commercial antistatic agent). The purpose of used avivage agent is to smoothen the fiber surface and prevent electrostatic charging of fibers.[11] Avivage agent was also used in order to reduce fibers from sticking to each other during spooling, but the effect was minimal.

3.4 | Surface of the melt spun fibers

The smoothness of the fiber surface also describes the fiber quality.[8] Therefore, the surface and cross-section morphology of melt spun cellulose fiber was studied using SEM. Both the cross-sectional surface cut and the

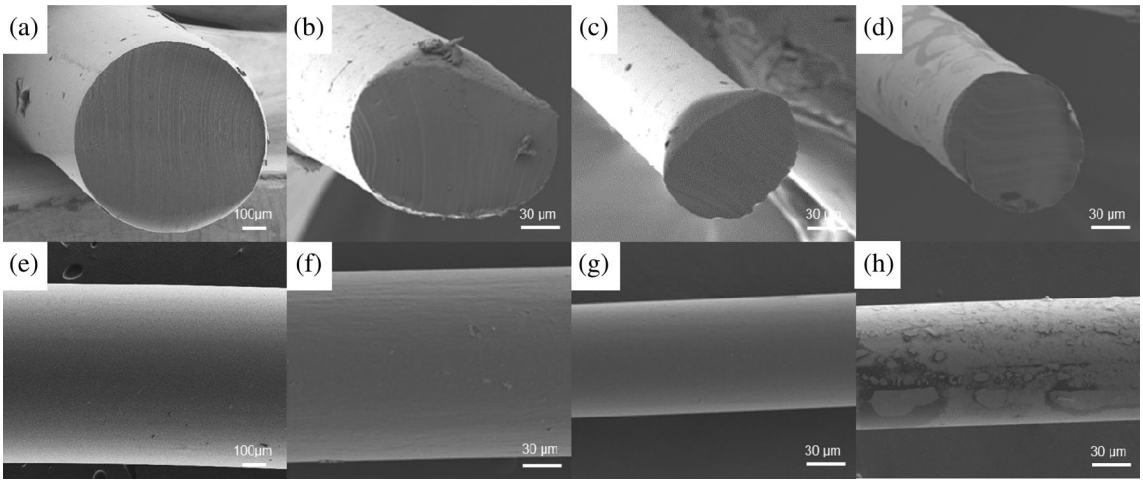

FIGURE 7 Scanning electron microscopic (SEM) image of the cross-section of the fibers using drawing speed of (a) 0 m/min, (b) 60 m/min, (c) 160 m/min, and (d) 160 m/min with avivage agent and surface of the fibers using drawing speed of (e) 0 m/min, (f) 60 m/min, (g) 160 m/min, and (h) 160 m/min with avivage agent. For fibers (a) and (e), 80× magnification was used, and for fibers (b), (c), (d), (f), (g), and (h), 250× magnification was used

TABLE 2 Mechanical properties of melt spun cellulose octanoate fibers

Drawing speed (m/min)	Avivage agent	Diameter[j] (µm)	Draw ratio (DR)	Linear density (dtex)	Tenacity (cN/dtex)	Elongation (%)
0	No	760.0 ± 2.5	0	4,177.2 ± 7.6[a]	0.17 ± 0.03[a]	223.0 ± 30.6[a]
60	No	175.8 ± 1.4	19	213.3 ± 6.7[b,c]	0.27 ± 0.03[c,d,e]	6.4 ± 0.6[e]
60	Yes	204.6 ± 0.8	15	250.2 ± 37.6[b]	0.19 ± 0.07[a]	22.6 ± 7.3[b]
80	No	123.3 ± 1.1	38	199.4 ± 23.5[c]	0.20 ± 0.02[a,b]	6.4 ± 0.4[e]
80	Yes	156.4 ± 0.7	24	182.4 ± 0.6[c]	0.27 ± 0.03[c,d]	20.5 ± 3.8[b,c]
100	No	118.4 ± 0.2	42	118.6 ± 4.6[d]	0.24 ± 0.03[b,c]	12.7 ± 0.9[c,d,e]
100	Yes	124.7 ± 0.5	37	118.7 ± 3.3[d]	0.29 ± 0.03[d,e,f]	15.5 ± 2.8[b,c,d]
120	No	104.1 ± 0.7	53	89.0 ± 4.3[d,e]	0.27 ± 0.03[c,d,e]	11.6 ± 2.5[d,e]
120	Yes	118.8 ± 0.3	42	97.5 ± 3.0[d,e]	0.33 ± 0.08[f,g,h]	13.8 ± 3.2[c,d,e]
140	No	97.3 ± 0.3	61	75.8 ± 5.1[d,e]	0.28 ± 0.02[d,e]	9.6 ± 2.1[d,e]
140	Yes	105.5 ± 0.4	52	93.5 ± 4.9[d,e]	0.31 ± 0.03[e,f,g]	12.8 ± 3.3[c,d,e]
160	No	88.9 ± 0.6	73	68.6 ± 1.8[e]	0.30 ± 0.02[d,e,f]	8.0 ± 0.9[d,e]
160	Yes	97.9 ± 0.6	60	65.7 ± 2.9[e]	0.38 ± 0.06[i]	10.7 ± 2.7[d,e]
180	No	83.2 ± 0.4	84	64.8 ± 5.1[e]	0.30 ± 0.02[d,e,f,g]	7.5 ± 1.0[d,e]
180	Yes	85.0 ± 0.6	80	65.9 ± 0.6[e]	0.36 ± 0.03[h,i]	9.5 ± 2.5[d,e]
200	No	77.2 ± 0.4	97	61.0 ± 5.8[e]	0.34 ± 0.04[g,h,i]	8.8 ± 2.4[d,e]
200	Yes	82.1 ± 0.7	86	63.2 ± 4.7[e]	0.35 ± 0.02[h,i]	9.8 ± 1.9[d,e]

[a-i]Means in same column with different superscripts are significantly different ($p < .05$). Number of samples for diameter and tensile measurements are $n = 5$ and $n = 20$, respectively.
[j]According to scanning electron microscopic (SEM) images.

surfaces of fibers were imaged. Due to the significant difference in the thickness between undrawn and drawn fibers, different magnifications were used; 80× magnification was used for undrawn fiber and 250× magnification for drawn fibers. According to the SEM results (Figure 7), the cross-section of cellulose octanoate fibers was very uniform and no porosity was observed. This indicates that cellulose octanoate was thoroughly melted during melt spinning process at 130°C without gasses or large impurities. Also, the fiber surfaces were very smooth and only minor surface roughness can be observed. This can result from the die exit as well as from instabilities during

drawing.[8] However, small nicks caused by sample handling cannot be completely ruled out. The used avivage agent was also observed in the SEM images (Figure 7d,h), causing blotches on the fiber surface. This indicates that the amount of avivage agent used could be lower. However, in this research, the amount of used avivage agent was deliberately kept relatively high in order to better visualize its effect.

3.5 | Mechanical properties of melt spun fibers

Tenacity and elongation at break are widely used to characterize the mechanical properties of melt spun fibers. Properties of fibers depend on both the inherent properties of material and processing parameters.[8] All cellulose octanoate fibers were spun using the same processing parameters, therefore only fiber drawing speed and used avivage agent has a possible effect on mechanical properties. It is also known that the mechanical properties (e.g., tenacity and elongation) of fibers mainly depend on the molecular chain orientation.[22,23] In the undrawn state, the low orientation of the molecular chain gives the spun filament a low strength.[11]

The diameter of the fibers was determined from SEM images. The diameter values (Table 2) indicate that the used avivage agent has an effect on the diameter of fibers. The diameter of fibers with avivage agent is about 10–30 μm thicker than the fibers without avivage agent, and this effect seems to be higher when using low drawing speeds. It is likely that the avivage agent has built up on the fiber surface and increased the diameter. Additionally, the avivage agent dosing pump was kept at constant speed throughout the drawing speed scan. Therefore, on lower drawing speeds the dose on the fiber is higher, causing more buildup.

Undrawn fiber had a very high linear density (4,177 dtex) but lowest tenacity at 0.17 cN/dtex. When the fibers were drawn, the linear densities decreased significantly in proportion to the drawing speed. The tenacity of drawn fibers varied between 0.19 and 0.38 cN/dtex (Table 2) and tenacity slightly increased when the linear density was decreased. When avivage agent was used, the tenacity was somewhat higher than without the avivage agent. The used avivage agent may plasticize the fiber material, allowing the molecules to orient more before breaking resulting in a slightly better tenacity and elongation values. The elongation value of undrawn fiber was quite high, 223%, while the elongation of drawn fibers varied between 6.4 and 22.6%. These values decreased with increasing drawing speed and decreasing linear density. This is in line with earlier reported[24] that elongation values of fibers depended mainly on the draw ratio. The biggest difference between elongation values was observed when 60 and 80 m/min drawing speed with and without avivage agent were used. When avivage agent was used, the elongation was three times higher compared with the values without avivage agent. At higher drawing speeds (>100 m/min), the effect of avivage agent was lower possibly due to the overall lower amount of avivage agent on the fiber. Based on these results we can conclude that by choosing the appropriate drawing speeds the final mechanical properties can be tuned.

The mechanical properties of the demonstrated cellulose ester fibers were compared with commercially available fibers such as PP and CAB. The mechanical properties of PP depend greatly on its quality and the processing conditions. In the literature,[25–27] tensile strength values for PP have been reported to be on the range of 0.5–26 cN/dtex and elongation to break values 40–900%.

Hooshmand et al.[4] have studied cellulose-based melt spun fibers. They have reported that CAB fibers with 15 wt% TEC have 21% elasticity. Wang et al.[10] have also reported that CAB fibers have 0.80 cN/dtex tenacity and 29% elongation, when spinning draw ratio of 10 was used. When spinning draw ratio was increased to 104, the tenacity was 1.06 cN/dtex. At the same time, elongation decreased to 13%. Based on these results, cellulose octanoate fibers in this research have quite similar elongations, but weaker tenacity values than CAB fibers. However, cellulose octanoate fibers were melt-spun without any plasticizers, whereas in case of CAB, TEC was needed. By using additives in the fibers, the processability, and mechanical properties of the fibers can be adjusted in the desired direction. However, the use of plasticizers has also challenges, such as migration, evaporation, and degradation of plasticizers under certain conditions, which can cause negative impacts to thermomechanical properties of fibers and contamination of the surrounding medium.[28,29]

4 | CONCLUSIONS

We have shown in practice that cellulose fatty acid esters can be used to melt spin textile fibers. The spinnability depends not only on the applied fatty acid type but also on the DS of cellulose esters. While mechanical properties of the produced fibers are not yet as good as those reported for commercial PP monofilament fibers, they are somewhat more comparable to other cellulose ester-based fibers. In addition, the comparable properties are

achieved without any plasticizers, which is clearly a benefit. The results still indicate that these novel cellulose ester-based fibers could provide a renewable and recyclable alternative, for example, PP in several technical and hygienic textile applications in the future.

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ORCID

Pia Willberg-Keyriläinen https://orcid.org/0000-0001-5990-5785

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